A Photoelectron Spectroscopic Study of Iron Pentacarbonyl

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INTRODUCTION

We have performed an angular and energy dependent photoelectron spectroscopic study of $Fe(CO)_5$ on beamline 10.0.1 of the Advanced Light Source using a Scienta electron energy analyzer system. Valence ionization electron spectra were recorded at a number of photon energies and at two different angles with respect to the polarization vector of the synchrotron radiation.

RESULTS

The complete photoelectron spectrum of $Fe(CO)_5$ obtained utilizing 40 eV synchrotron photons at an overall resolution of ~26 meV and at an angle of 54.7° is presented in Fig. 1.

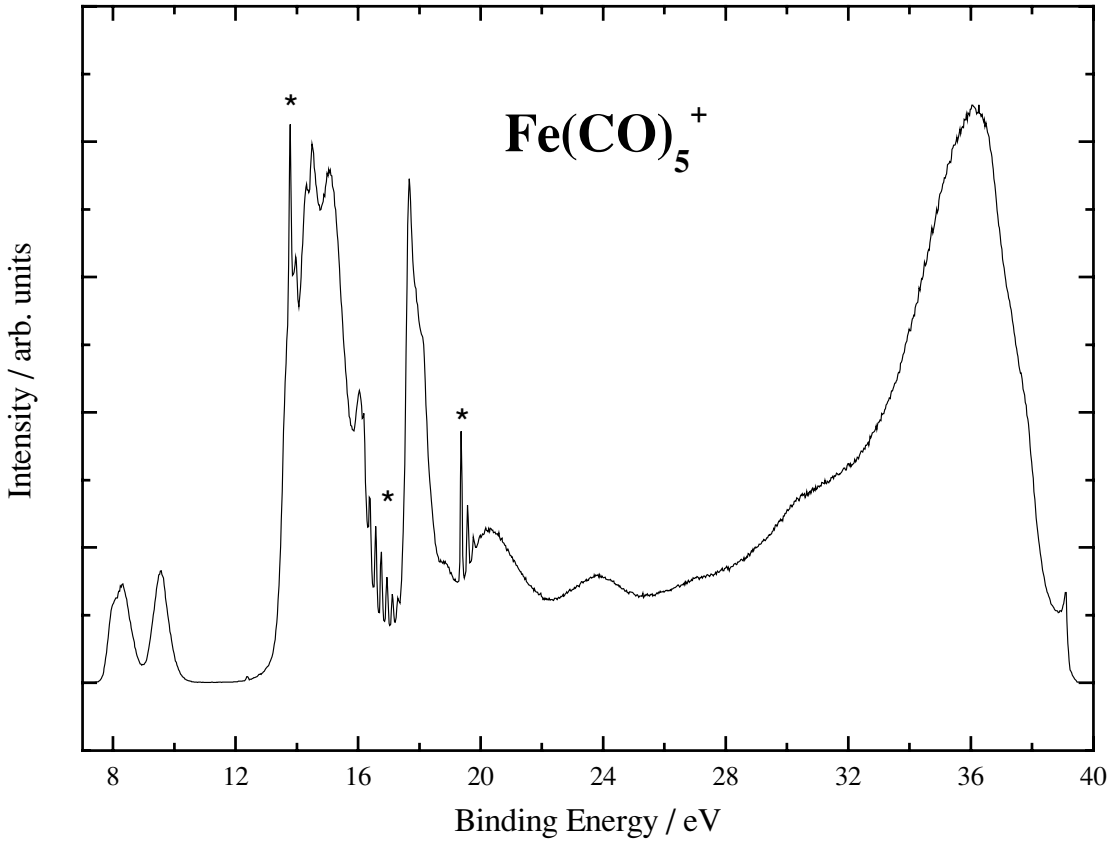

Figure 1. Photoelectron spectrum of $Fe(CO)_5$.

The spectrum shown in Fig. 1 is uncorrected for the transmission function of the electron spectrometer and most likely results in the appearance of the prominent broad feature at about 36 eV. The sharp features marked with asterisks in Fig. 1 are due to gaseous CO that apparently forms from the decomposition of $Fe(CO)_5$ in the heated (50^o C) stainless steel sample transfer line to the photoionization apparatus. The persistent presence of CO^+ peaks in all our spectra, although troublesome, did serve for energy calibration purposes. The two peaks at low binding energy (7-10.5 eV) have been identified[1,2] as being due to molecular orbitals primarily made up from contributions of the Fe 3d atomic orbitals. The band structure in Fig. 1 between 13 and 26 eV is primarily due to the CO ligands and has been studied theoretically and experimentally on numerous occasions.[1-5]

In Figs. 2 and 3 we present the photon energy dependent photoelectron spectra collected at two different angles (0^o and 54.7^o, respectively) relative to the polarization vector of the synchrotron radiation. Only minor differences are noticed between the spectra taken at the same photon energy but at different angles. The most dramatic effects are seen in the energy dependence at a given detection angle with both angle series showing similar results. They are as follow. The band systems centered on 18 eV increase relative to the band systems between 13 and 17 eV as the excitation energy increases. The former systems have been attributed to ionization from ligand 4σ-type orbitals while the later are primarily associated with the 5σ and 1π orbitals of CO.[4] In a similar way, the intensity of the two low lying band systems increases relative to the band systems between 13 and 17 eV as the excitation energy is increased. Furthermore, the relative intensity of the two low lying bands changes as the photon energy changes with the second band system being favored at the higher excitation energy. This later effect has been studied at higher overall electron energy resolution (~6 meV) as demonstrated in Fig. 4. As can be seen in Fig. 4, the lowest energy band feature is made up of the superposition of two peaks that have been identified with two Jahn-Teller split electronic states.[3] All these differences we observe are attributed to changes in the photoionization cross section as a function excitation energy. However, before we attempt to quantify and identify these effects more specifically we need to produce transmission corrected photoelectron spectra. This procedure is currently underway.

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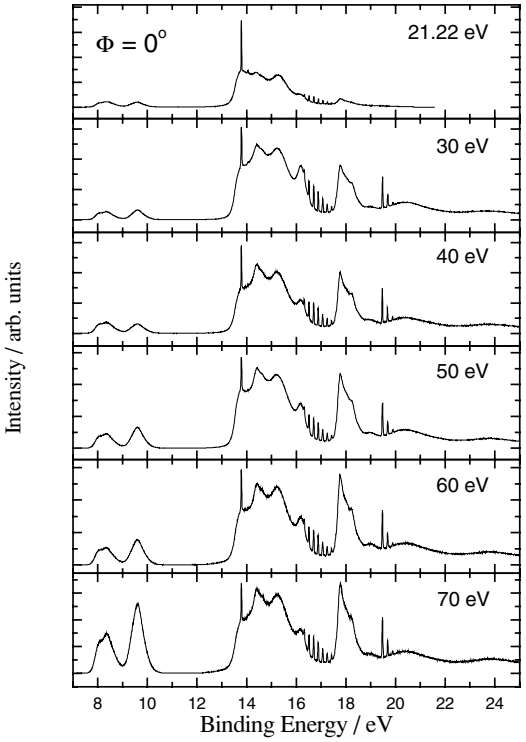

Figure 2. Energy dependence of the PE specturm of $Fe(CO)_5$ at 0^o detection angle.

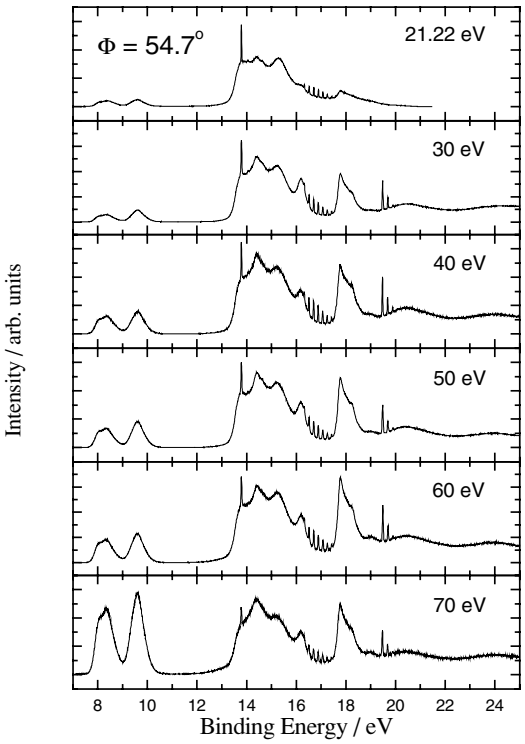

Figure 3. Energy dependence of the PE spectrum of $Fe(CO)_5$ at 54.7^o detection angle.

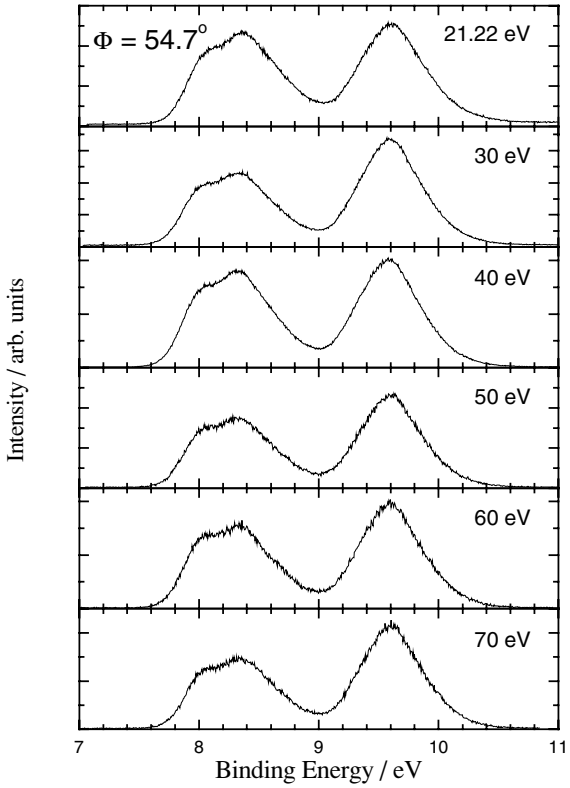

Figure 4. Energy dependence of the low-energy portion of the PE spectrum of $Fe(CO)_5$ at 54.7^o detection angle.